

Non-adiabatic dynamics in SO₂: II. The role of triplet states studied by surface-hopping simulations

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The importance of triplet states in the photorelaxation dynamics of SO₂ is studied by mixed quantum-classical dynamics simulations. Using the Surface Hopping including ARbitrary Couplings (SHARC) method, intersystem crossing processes caused by spin-orbit coupling are found occurring on an ultrafast time scale (below 100 fs) and thus competing with internal conversion. Comparing the dynamics including singlet and triplet states to the singlet-only dynamics, very different results are obtained for the populations of the respective states. However, the vibrational motion in the triplet manifold very much resembles the one in the singlet manifold. Consequently, the contribution of the triplet states may be difficult to detect in a broad range of experiments.

I. INTRODUCTION

Sulphur dioxide is an attractive molecular system which combines a very small system size with many different excited states coupled in a complex way, offering a challenging photodynamics which can be studied with ultra-fast, time-resolved spectroscopic methods and modern high-level ab initio techniques.

In a companion paper,¹ (hereafter referred to as paper I) the experimental and theoretical efforts of the last 80 years to characterize the electronic excited states of SO₂ have been surveyed in detail. Already in the 1930s,^{2,3} high-resolution absorption spectra of SO₂ were recorded. The absorption spectrum features three prominent bands in the near- and medium-UV range, named the forbidden band and the first and second allowed bands.⁴ Especially the first allowed band between 3.6 eV and 5.1 eV was subject to numerous analyses (reviewed by Herzberg⁵ and Heicklen et al.⁴) because of its intricate structure. From a modern point of view, this band system arises from the transition from the ground state to the vibronically coupled $1^1A_2/1^1B_1$ system (the two lowest excited singlet states). Müller and Köppel⁶ treated this singlet state system using full-dimensional quantum dynamics (QD) and found that the system remains primarily on the lower adiabatic potential energy surface (PES) after excitation. An extension of this study has been published very recently.⁷

However, there is significant evidence^{8–11} that the excited state dynamics within the first allowed band system is also affected by the presence of triplet states. SO₂ shows in the region between 3.1 eV and 3.6 eV a weak absorption profile (the forbidden band), which was shown to arise from excitation to triplet states by Douglas¹² by means of the Zeeman effect. Even though the number, location and character of the triplet states could not be determined by early spectroscopic means, modern ab ini-

tio methods showed that three states of 3A_2 , 3B_1 and 3B_2 symmetry are present at energies slightly lower than the corresponding singlet states. Consequently, intersystem crossing (ISC) between singlet and triplet states could be plausible and the photodynamics of SO₂ might be influenced by both ISC and internal conversion (IC) processes.

Very recently, both spectroscopic^{13–18} and theoretical^{19–21} studies suggested that in a number of systems ISC indeed can compete with IC on an ultrafast time scale. In order to provide more evidence for these new findings, several experimental methods based on high-resolution time-resolved spectroscopy have been developed.^{22–28} Further experimental indications for the case of SO₂ can be found in paper I.

In the present paper, we attempt to unravel the excited state dynamics of SO₂ theoretically. To this aim, ab initio surface hopping molecular dynamics (MD) is employed using the SHARC code.²⁹ SHARC (Surface Hopping including ARbitrary Couplings) can treat IC and ISC, mediated by non-adiabatic couplings and spin-orbit couplings, respectively, on the same footing. This is achieved by performing surface hopping in a basis of spin-orbit-coupled electronic states, which are obtained by diagonalization of the potential energy matrix including the spin-orbit couplings. The simulations are focused on the energy range corresponding to the forbidden and first allowed band of the experimental absorption spectrum.³⁰ The applicability of SHARC on SO₂ is validated by running also trajectories on the singlet-manifold only, whose results are compared with those obtained by Müller and Köppel using accurate quantum dynamical (QD) calculations.⁶ Other applications of SHARC can be found in Refs. 29, 31–33.

II. METHODOLOGY

In the following, a brief summary of general surface hopping method as well as the specific SHARC variant is given. Further details on SHARC can be found in Ref. 29. A summary of the employed ab-initio methods and initial

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conditions generation is also given below.

A. Surface hopping

The widely applied fewest switches criterion for surface hopping was devised by Tully in 1990.³⁴ It allows incorporating non-adiabatic effects into semi-classical *ab initio* dynamics,³⁵ where the nuclei can be propagated on only one PES at a time, by means of state hops according to jumping probabilities. To this end, the electronic wavefunction is expanded in the basis of adiabatic eigenstates $|\psi_\alpha\rangle$ of the Hamiltonian:

$$|\psi\rangle = \sum_{\alpha} c_{\alpha} |\psi_{\alpha}\rangle. \quad (1)$$

The state coefficients c_{α} are obtained by numerical integration of the time-dependent Schrödinger equation:

$$\frac{\partial}{\partial t} c_{\beta} = - \sum_{\alpha} c_{\alpha} [i\delta_{\beta\alpha} E_{\alpha}^a + \mathbf{v} \cdot \mathbf{T}_{\beta\alpha}], \quad (2)$$

where \mathbf{v} is the velocity vector, E_{α}^a is the adiabatic energy of state α and

$$\mathbf{T}_{\beta\alpha} = \langle \psi_{\beta} | \nabla_{\mathbf{R}} | \psi_{\alpha} \rangle \quad (3)$$

is the non-adiabatic coupling vector.

Based on the state coefficients, the hopping probabilities from the current state into any other state can be computed according to:

$$P_{\beta \rightarrow \alpha} = \frac{2\Delta t}{c_{\beta}^* c_{\beta}} \Re(c_{\beta}^* c_{\alpha} [iH_{\beta\alpha} + \mathbf{v} \cdot \mathbf{T}_{\beta\alpha}]). \quad (4)$$

B. Surface hopping including arbitrary couplings

In the scheme outlined above, the electronic Hamiltonian was assumed to be diagonal in the basis of the wavefunctions $|\psi_{\alpha}\rangle$. If perturbation terms are added to the Hamiltonian, off-diagonal elements between the states under consideration may be introduced:

$$H_{\beta\alpha}^{(1)} = H_{\beta\alpha}^{(0)} + \langle \psi_{\beta}^{(0)} | \hat{H}^{(1)} | \psi_{\alpha}^{(0)} \rangle. \quad (5)$$

Such perturbations include for example spin-orbit coupling, but also the interaction with laser fields. Within the SHARC algorithm, the Hamiltonian $H_{\beta\alpha}^{(1)}$ is diagonalized by an unitary transformation. To obtain a consistent adiabatic picture, the non-adiabatic couplings are transformed into the new basis $\{|\psi_{\alpha}^{(1)}\rangle\}$ according to:

$$\mathbf{T}_{\beta\alpha}^{(1)} = (\mathbf{U}^{\dagger} \mathbf{T}^{(0)} \mathbf{U})_{\beta\alpha} + (\mathbf{U}^{\dagger} \nabla \mathbf{U})_{\beta\alpha}, \quad (6)$$

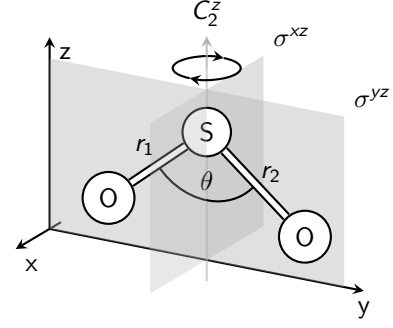


FIG. 1. Geometry of the molecule, internal coordinates and symmetry elements of SO_2 . The experimental values are $r_1=r_2=1.432\text{\AA}$ and $\theta=119.5^\circ$.

so that the final equation for the evolution of the state coefficients is

$$\begin{aligned} \frac{\partial}{\partial t} c_{\beta} = - \sum_{\alpha} c_{\alpha} \left[i(\mathbf{U}^{\dagger} \mathbf{H} \mathbf{U})_{\beta\alpha} \right. \\ \left. + \mathbf{v} \cdot (\mathbf{U}^{\dagger} \mathbf{T}^{(0)} \mathbf{U})_{\beta\alpha} + \left(\mathbf{U}^{\dagger} \frac{\partial}{\partial t} \mathbf{U} \right)_{\beta\alpha} \right], \quad (7) \end{aligned}$$

The motion of the nuclei is governed by gradients obtained numerically from the unperturbed gradients under the approximation of constant spin-orbit coupling elements, which is a good approximation as long as the coupling elements or their change are small. To date no analytical gradients for spin-orbit-perturbed states are available, but work is in progress.³⁶

Using the described unitary transformation, the obtained states are not spin-pure states anymore because singlets and triplets mix via spin-orbit coupling. However, in the basis of spin-orbit-coupled electronic states, IC and ISC are not fundamentally different anymore³⁷ and can be conveniently investigated using non-adiabatic dynamics.

C. Ab initio methods

Throughout this paper, the nuclear motion of SO_2 is discussed in terms of a set of internal coordinates consisting of the average bond length, r_{sym} , one half of the bond length difference, r_{asym} , and the bond angle, θ :

$$r_{\text{sym}} = \frac{1}{2}(r_1 + r_2), \quad r_{\text{asym}} = \frac{1}{2}(r_1 - r_2), \quad (8)$$

where r_1 , r_2 and θ are defined in figure 1. The MD calculations themselves were carried out in cartesian coordinates.

The on-the-fly electronic structure calculations required for the MD simulations were performed with the MOLPRO 2010.1 package,³⁸ which was interfaced to SHARC. In order to achieve a description of the

electronic states that is both feasible and accurate, we used the Complete Active Space Self-Consistent Field (CASSCF)³⁹ approach combined with the def2-SVP⁴⁰ basis set to obtain preliminary wavefunctions of the three lowest-lying singlet and three lowest-lying triplet states. The employed active space comprises 12 electrons in 9 orbitals, so that this prescription is denoted as CASSCF(12,9)/def2-SVP. State-averaged calculations with equal weights were performed either on the three singlet states or the total six (three singlet and three triplet) electronic states. The so-obtained wavefunctions were subsequently correlated using MOLPRO's internally contracted multireference configuration interaction (MRCI) formalism.⁴¹ The MRCI method was found to be necessary since the CASSCF potentials are otherwise too flat for large bond lengths – a fact already noted by Katagiri et al.⁴² For the MRCI reference space, the three lowest active orbitals were constrained to contain at least 5 electrons, while the three highest active orbitals were constrained to a maximum of two electrons. To further speed up the calculations, configurations containing exactly one electron in the external orbital space were omitted. The spin-orbit matrix elements were calculated using the effective Fock-type spin-orbit operator⁴³ implemented in MOLPRO.

D. Gradient modifications

Since MOLPRO is not able to calculate MRCI gradients analytically, approximate MRCI gradients were obtained from the CASSCF ones. The component of the CASSCF gradient in the direction of the trajectory's current motion was substituted by a term obtained from the MRCI energy difference of the last and the current trajectory step. The new gradient reads as follows:

$$\mathbf{g} = \mathbf{g}_{\text{CAS}} + \left[\frac{E(\mathbf{R}_i) - E(\mathbf{R}_{i-1})}{\Delta \mathbf{R} \cdot \Delta \mathbf{R}} - \frac{\mathbf{g}_{\text{CAS}} \cdot \Delta \mathbf{R}}{\Delta \mathbf{R} \cdot \Delta \mathbf{R}} \right] \Delta \mathbf{R}, \quad (9)$$

where \mathbf{g}_{CAS} is the gradient of the CASSCF energies, $E(\mathbf{R}_i)$ and $E(\mathbf{R}_{i-1})$ are the MRCI energies of the current and last step, respectively, and $\Delta \mathbf{R} = \mathbf{R}_i - \mathbf{R}_{i-1}$ is the displacement vector between the last and current geometry.

In order to account for total energy conservation (despite small remaining inconsistencies), the kinetic energy is scaled after each step. To accomplish this, the kinetic energy of each atom A is recalculated according to:

$$E_{\text{kin},A}^{\text{scaled}} = \frac{E_{\text{kin},A}}{\sum_A E_{\text{kin},A}} \cdot (E_{\text{tot}} - E_{\text{pot}}). \quad (10)$$

Here, $E_{\text{tot}} - E_{\text{pot}}$ is the kinetic energy required by energy conservation. The kinetic energy is divided among the atoms proportionally to the unscaled kinetic energies. With the scaled kinetic energies, the velocity vectors of

each atom A were recomputed as follows:

$$\mathbf{v}_A^{\text{scaled}} = \sqrt{2 \frac{E_{\text{kin},A}^{\text{scaled}}}{M_A}} \cdot \frac{\mathbf{v}_A}{|\mathbf{v}_A|}. \quad (11)$$

In this way, the directions of the velocity vectors are not changed. The nuclear motion according to these gradients was determined with the Velocity-Verlet algorithm⁴⁴ using a time-step of 0.5 fs.

E. Initial conditions

The generation of the initial geometries and velocities was carried out with the NEWTON-X program suite.^{45,46} A quantum harmonic oscillator Wigner distribution^{47,48} was generated using numerical frequencies obtained with RI-MP2⁴⁹ and the basis set cc-pVTZ, as implemented in the TURBOMOLE 6.2 suite.⁵⁰

The obtained initial conditions displayed bond lengths between 1.36 Å and 1.54 Å and bond angles between 110 ° and 128 °. The initial kinetic energies showed an average of 0.09 eV, with a maximum of 0.5 eV.

All trajectories started in one of the excited states at $t=0$, which is equivalent to a delta pulse excitation. The initially populated state was determined stochastically based on computed transition probabilities $P_{0\alpha}$ according to:

$$P_{0\alpha} = \frac{f_{0\alpha}}{E_{0\alpha}^2} \cdot \left[\sum_{\beta}^{\text{States}} \frac{f_{0\beta}}{E_{0\beta}^2} \right]^{-1}, \quad (12)$$

where $E_{0\alpha}$ is the energy difference between ground state and state α and $f_{0\alpha}$ is the oscillator strength for this transition. For the determination of the initial state, for each initial geometry one state in the energy band between 3.5 eV and 5.5 eV was chosen based on the probabilities $P_{0\alpha}$. The state coefficient of state c_{α} was set equal to 1 and $c_{\beta \neq \alpha}$ equal to 0.

III. RESULTS

A. State terminology

To compare theoretical results to experimental findings, a note on nomenclature is in order, since spectroscopic results are usually discussed in terms of diabatic states (where the wavefunction character is preserved), while ab initio MD simulations typically employ adiabatic states (where the potential coupling between states vanishes).⁵¹

Figure 2 shows the PESs of the lowest-lying five adiabatic states that are relevant to the dynamics. Exemplarily, the PES are shown in the $(r_{\text{asym}}, \theta)$ space. SO₂ exhibits C_{2v} symmetry if $r_{\text{asym}} = 0$; otherwise, the point

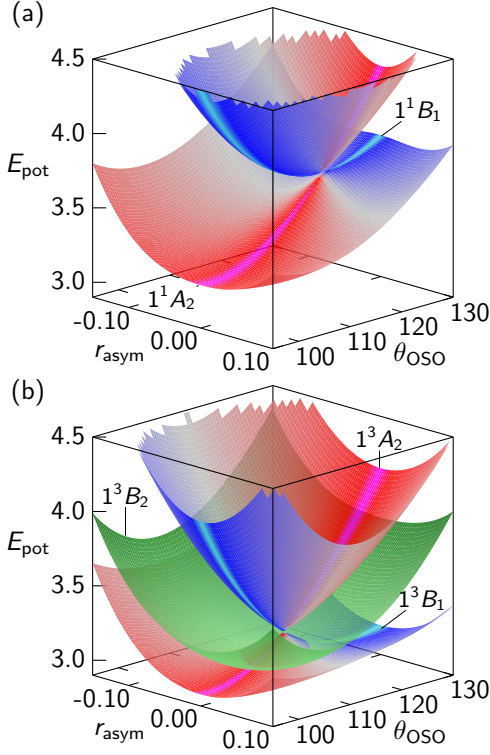


FIG. 2. PESs of (a) singlet states S_1 (lower surface) and S_2 (upper surface) and (b) of triplet states T_1 (lowest), T_2 (intermediate), and T_3 (highest). Colors indicate the wavefunction character of the adiabatic states, where purple corresponds to 1^1A_2 or 1^3A_2 , cyan to 1^1B_1 or 1^3B_1 and green to 1^3B_2 . For $r_{\text{asym}} \neq 0$, the dominating character is indicated by red (A_2), blue (B_1) or grey (mixed).

group changes C_s . Within C_{2v} symmetry, all the considered electronic states have different state symmetry and hence do not mix. The diabatic singlet states have state symmetry 1^1A_2 and 1^1B_1 and are shown in purple and cyan, respectively, in figure 2 (a). For the remaining parts of the PESs, where $r_{\text{asym}} \neq 0$, both singlet states have symmetry A'' . Consequently, the two diabatic states mix and give rise to the two adiabatic states S_1 (lower surface) and S_2 (upper surface), which are used in the MD simulation. However, the contribution of the diabatic states to these mixtures depends on the geometry. We have indicated the predominant wavefunction character of the adiabatic (mixed) states at each point. Red corresponds to the character of the 1^1A_2 state and blue to the one of 1^1B_1 .

The same color scheme is used for the triplet states, shown in figure 2 (b). Additionally, the state $1^3B_2/1^3A'$ is shown in green. Since even in C_s symmetry this state does not mix with the A'' states, it retains its wavefunction character along the whole surface. The adiabatic triplet states used in the MD simulations are called T_1 , T_2 and T_3 and are obtained from $1^3A''$, $2^3A''$ and $1^3A'$ by ordering the states strictly according to the energy at each geometry. For example, the T_2 consists of the visi-

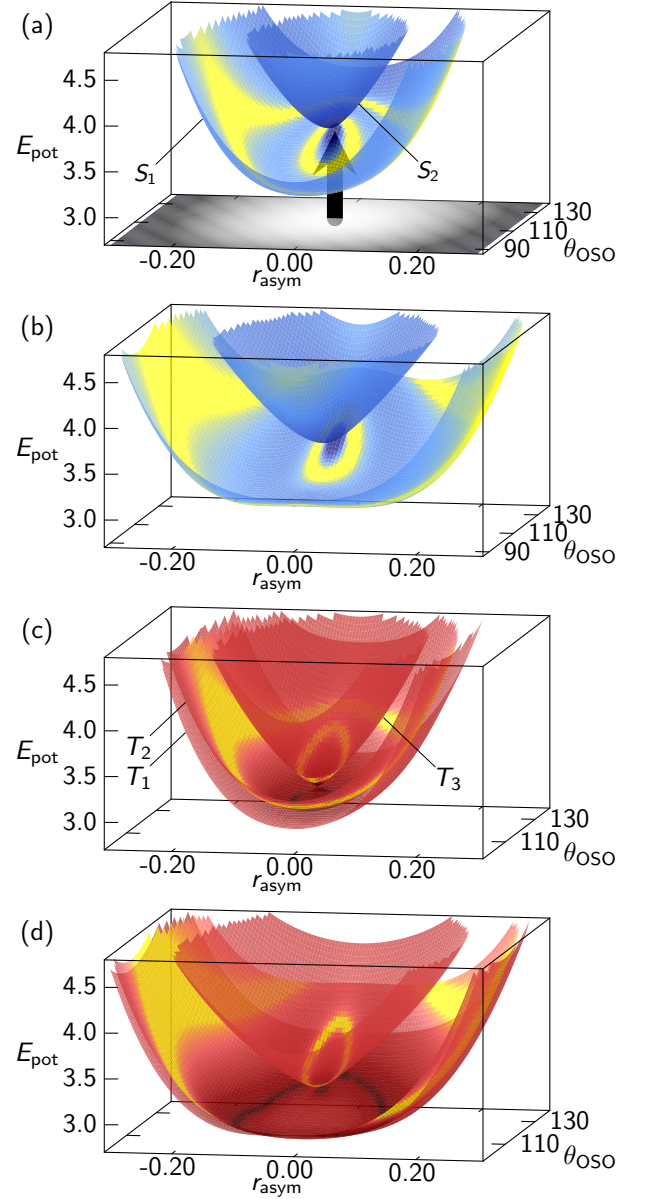


FIG. 3. PESs of the two lowest excited singlet surfaces for $r_{\text{sym}}=1.5$ Å (a) and $r_{\text{sym}}=1.7$ Å (b). PESs of the three lowest triplet surfaces for $r_{\text{sym}}=1.5$ Å (c) and $r_{\text{sym}}=1.7$ Å (d). The ground state is given as a grey-scale contour map in panel(a) and the Franck-Condon point is indicated by an arrow. Darker shades of blue (for singlets) or red (for triplets) indicate a stronger non-adiabatic coupling between the respective states. Singlet-triplet interaction regions (energy difference < 0.05 eV ≈ 400 cm $^{-1}$) are indicated in yellow.

ble part of the green surface and the lower cone (pointing upwards) situated energetically above the green surface.

B. Potential energy surfaces

In figure 3, panels (a) and (b) depict the potentials of the two excited singlet states in the same coordinate space as in figure 2 but using different axis ranges. In panel (a), $r_{\text{sym}}=1.5$ Å, which is similar to r_{sym} at the ground state equilibrium geometry. The ground state energy is given as a greyscale contour to indicate the Franck-Condon region. In panel (b), $r_{\text{sym}}=1.7$ Å, which exemplarily represents the more stretched geometries found during the course of the MD simulation (see below). Regions of strong non-adiabatic coupling between the singlet states are shaded in dark blue, while yellow indicates regions where triplets are close to singlet states (less than 0.05 eV ≈ 400 cm $^{-1}$). In panels (c) and (d), the potentials of the three lowest-lying triplet states are shown analogously.

In both panels (a) and (b), the singlet states are connected via a conical intersection (CI) directly situated above the Franck-Condon region (in (a) at $\theta=118.5^\circ$ and $r_{\text{asym}}=0.0$ Å; in (b) at $\theta=120.0^\circ$ and also $r_{\text{asym}}=0.0$ Å). The S_2 surface forms a narrow funnel without any intersection with triplet states. In contrast, the S_1 intersects with all three triplet states. Close to the CI, the S_1 crosses with the T_3 , while T_1 and T_2 come close for larger values of r_{asym} . At large values for r_{sym} , the S_1 surface exhibits a double-minimum (see panel (b)).

Since the triplet states have basically the same wavefunction character as their corresponding singlet states, the PESs are very similar. In panel (c), the T_2/T_3 CI is located at $\theta=111.0^\circ$, $r_{\text{asym}}=0.0$ Å and in panel (d) at $\theta=113.5^\circ$, $r_{\text{asym}}=0.0$ Å.

C. Spectrum

Using the excitation energies $E_{0\alpha,j}$ and the dipole moments $\mu_{0\alpha,j}$ of the initial geometries of all trajectories j for all states α , an approximation to the absorption spectrum has been simulated via a Gaussian convolution:

$$g_\alpha(E) = \sum_j^{\text{trj}} f_{0\alpha,j} \cdot \exp\left(-\frac{(E - E_{0\alpha,j})^2}{2\epsilon^2}\right). \quad (13)$$

Here, $g_\alpha(E)$ is the part of the absorption spectrum arising from the transition from the ground state to state α , depending on the energy E . The parameter $\epsilon=0.027$ eV describes the width of the Gaussian broadening. The spectrum is based on the properties of 280 initial conditions.

The total absorption spectrum is the sum of $g_\alpha(E)$ over all states α . To account for the first allowed band of SO $_2$, only the two adiabatic states S_1 and S_2 need to be considered. The obtained total spectrum together with its contributions from the transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, as well as the experimental spectrum³⁰ are depicted in figure 4. Both spectra were normalized. The agreement

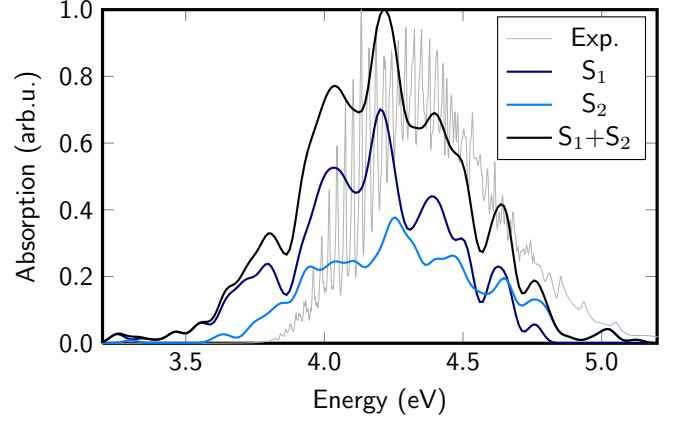


FIG. 4. Absorption spectrum arising from excitation to S_1 and S_2 (dark and light blue, respectively). The experimental spectrum of Golomb et al.³⁰ is given in grey.

between theory and experiment is satisfactory, considering the overall energy range and the general shape of the band, although the calculated spectrum is slightly red-shifted. The shape of the high-energy flank of the spectrum is well reproduced, while the low-energy flank gives too high oscillator strengths for energies below 3.9 eV. Naturally, the vibrational structure of the spectrum cannot be reproduced by this semi-classical method.

D. Dynamics in the singlet-manifold

In order to validate our method, we first performed a simulation of an ensemble of 42 trajectories, including only the three lowest-lying singlet states S_0 to S_2 . Thus, the results are directly comparable to those obtained by Müller and Köppel,⁶ using full-dimensional QD on pre-calculated PESs for S_1 and S_2 . The PESs used in their simulations were obtained from the earlier work of Weis.^{52,53}

Figure 5 shows the time-dependent populations of S_1 and S_2 as obtained by Müller and Köppel (grey curves). At $t=0$, both states are populated, but S_1 absorbs a larger fraction of the population. During the first femtoseconds, some small population fluctuations take place. After approximately 10 fs, the S_2 starts to transfer population to the S_1 and gets completely depopulated after 40 fs. After about 65 fs, again some population is transferred from S_1 to S_2 , because the wavepacket/ensemble returns to the interaction region of S_1 and S_2 near the Franck-Condon point.

Figure 5 also depicts the time evolution of S_1 and S_2 obtained with SHARC. As it can be seen, the initial population ratio obtained with SHARC is comparable to that predicted by QD. In the MD simulation, however, the population transfer from S_1 to S_2 is faster (during the first 5 fs). Starting at about 15 fs, the S_2 begins to continuously transfer population to the S_1 until the former

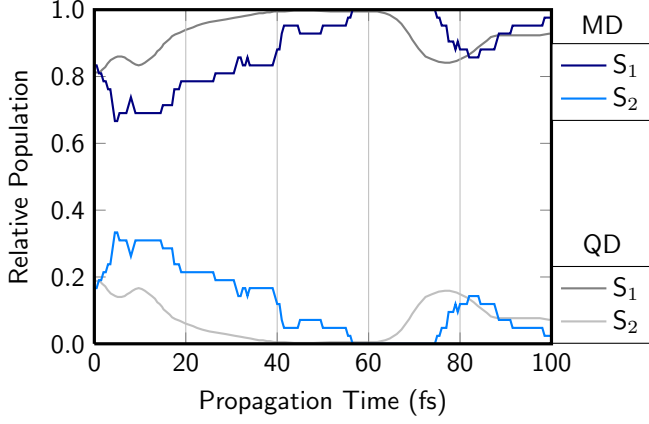


FIG. 5. Relative population of S_1 and S_2 in the QD simulation of Müller and Köppel (black and grey) and the corresponding results of an MD simulation including 42 trajectories (blue). Data taken from their paper.⁶

is completely depleted at around 60 fs. Between 70 and 80 fs the S_2 is repopulated, slightly delayed compared to the results of Müller and Köppel. By the end of the propagations (100 fs), both methods predict a similar population exchange between both electronic states. In summary, despite different levels of theory in the QD and the MD simulations, a satisfactory agreement is found between both methods.

E. Dynamics in the singlet-triplet manifold

Encouraged by the general agreement found in the dynamics performed within the singlet-manifold, an ensemble of 207 trajectories (171 starting in S_1 and 36 in S_2) was propagated for 800 fs, now allowing the interaction with triplet states. In the following analysis, special emphasis is put on the first 100 fs of the simulation.

Figure 6 displays the relative populations of all singlet and triplet states depending on time in logarithmic scale. For simplicity, the populations of the three M_S components of each triplet state were summed up. The colors denoting the states in figure 6 (singlet states in shades of blue, triplets in shades of red) are used consistently in all subsequent figures to allow for quick recognition of the respective state.

In accordance with dynamics on the singlet-manifold, the initial population ratio is approximately 0.8:0.2 for $S_1:S_2$. The triplet states are unpopulated initially (note that figure 6 starts at $t=1$ fs). However, the course of the dynamics shows remarkable differences with respect to the singlet-only case. Already after less than 10 fs, the population of S_1 and – to a lesser extent – S_2 decreases, while the one of T_3 increases. The lower-lying T_1 and T_2 are populated only after around 30 fs. At the same time, the population of S_1 is diminished substantially. For later times, the states' populations fluctuate around

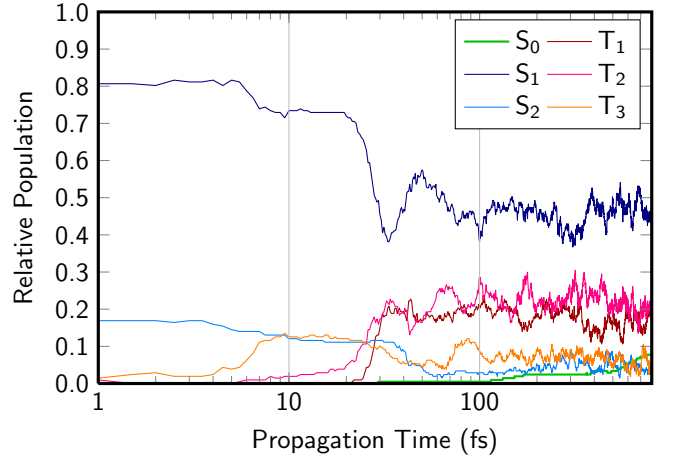


FIG. 6. Relative population of the six states in the dynamics simulation including triplet states.

some mean value: S_1 keeps about 50% of the total population, T_1 and T_2 keep 20% each, and S_2 and T_3 the remainder. During the course of the simulation, also a small number of trajectories relaxed to the ground state S_0 .

In order to obtain a detailed interpretation of the state interactions, the numbers of trajectories hopping from state β to state α at time step t_n , denoted $\Delta N_{\beta\alpha}(t_n)$, are analyzed. We use a Gaussian convolution in order to convert the discrete $\Delta N_{\beta\alpha}(t_n)$ into more comprehensible, continuous data. The obtained “density of state hops” at time t is

$$\mathcal{N}_{\beta\alpha}(t) = \sum_n \Delta N_{\beta\alpha}(t_n) \cdot \exp\left(-\frac{(t_n - t)^2}{2\tau^2}\right), \quad (14)$$

with a broadening parameter of $\tau=5$ fs. In the data so depicted, the area under the curves of $\mathcal{N}_{\beta\alpha}(t)$ is proportional to the number of state hops in a given time interval. The density of state hops is given in figure 7 for the first 300 fs.

Additionally, in order to extract time constants for the population transfer rate, we cumulate the number of state hops and fit all early transfer events separately using exponentials and all later (> 100 fs) according to zero-order kinetics (for an explanation of this distinction between early and late events, see below).

Figure 7a shows the interaction of S_2 with S_1 . Directly after the start of the simulation and again after approximately 35 fs, S_2 transfers population to S_1 . For later times, S_2 does not show notable interaction with S_1 . The fitting procedure gave time constants of 7 and 8 fs, respectively, for the two transfer events. Combined, 16% of all trajectories were transferred to S_1 .

T_1 gets populated from S_1 (panel (b)) after 30 fs and immediately afterwards the same amount of population is transferred back (boxes (2) and (3)). Consequently, during the first 100 fs, no net transfer from S_1 to T_1 is observed.

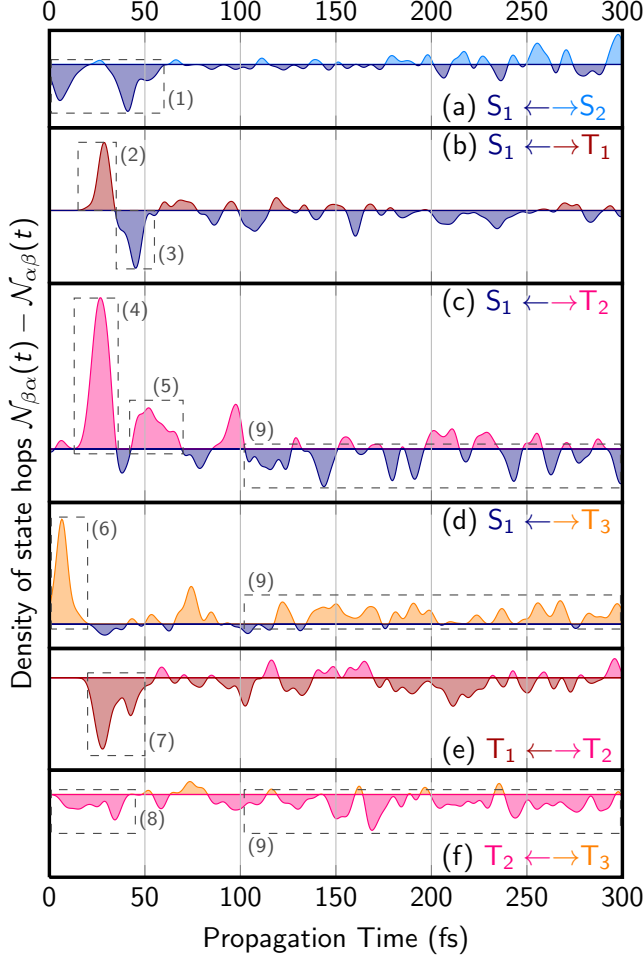


FIG. 7. Density of net hops between interacting pairs of states. Dashed boxes enclose events discussed in the text. Colors denote the direction of the population transfer as denoted in the labels. Common vertical scales have been used.

After 20 fs, S_1 transfers a large number of trajectories to T_2 (panel (c), box (4)) and again after 40 fs (box (5)). Treating the interval from 20 fs to 100 fs as one event, an effective time constant of 13 fs and a total transfer of 33% of all trajectories is found.

The interaction between states S_1 and T_3 in panel (d) provides the earliest ISC process. The transfer of population to T_3 (box (6)) starts immediately and during the first 100 fs, about 15% of all trajectories switch to T_3 with an effective time constant of 8 fs.

The states T_1 and T_2 also interact with each other, see panel (e). Box (7) shows a transfer from T_2 to T_1 , starting after 20 fs. The exponential fit of the cumulated net hops yields a time constant of 11 fs.

The last pair of states exhibiting notable interactions is T_3 and T_2 , which are connected via a CI similar to the one linking S_2 and S_1 . Panel (f) of figure 7 shows that the CI facilitates the ultrafast decay from T_3 to T_2 as soon as T_3 is populated. This process is slightly slower than the ones already mentioned, with an estimated time

constant of 17 fs.

The state interactions for later times than 100 fs exhibit characteristics very different from the early part of the simulation. S_2 and T_1 interact significantly less with S_1 . However, states S_1 , T_2 and T_3 exchange population in a circular fashion, shown in the three boxes labeled (9). This cycle consists of three steps, $T_2 \rightarrow S_1$ in panel (c), $S_1 \rightarrow T_3$ in panel (d) and $T_3 \rightarrow T_2$ in panel (f). The cumulated net hops of these three interactions for times greater than 100 fs were fitted according to zero-order kinetics. Time constants of 10, 13 and again 13%/100 fs (% of all trajectories per 100 fs) were found, respectively.

Figure 8 shows the evolution of the internal coordinates of all trajectories in all states. In panel (a), the dynamics in the asymmetric stretch mode is depicted. The lower-lying excited states S_1 , T_1 and T_2 all show a strong excitation of this mode. T_2 and T_1 get only populated once the S_1 trajectories has moved to large enough values of r_{asym} . All three states show almost exactly the same motion with regards to oscillation period and amplitude, thus we define these states as one group in the following discussion. On the contrary, a very different kind of motion is exhibited by S_2 and T_3 , which do not show any excitation of the asymmetric stretch mode. These two states therefore are classified as a second group.

The classification of the excited states into the groups S_1 , T_1 and T_2 on the one hand and S_2 and T_3 on the other hand is confirmed by the other modes. For the symmetric stretch mode in panel (b), an oscillation period of 70 fs and maximum r_{sym} of 1.8 Å is found for the first group, while the second group performs one oscillation in 45 fs with a maximum r_{sym} of slightly above 1.7 Å. The bending mode (panel (c)) of S_1 , T_1 and T_2 show a period of 70 fs and a minimum angle of 95°, the values of S_2 and T_3 are 45 fs and 105°.

IV. DISCUSSION

A. Potential energy surfaces

The excitation in SO_2 takes place from the 1^1A_1 ground state to the bright 1^1B_1 state. In the Franck-Condon region, this state crosses with 1^1A_2 and gives rise to a CI. Thus, in our adiabatic picture (see subsection III A) the bright state 1^1B_1 contributes to both S_1 and S_2 (for $\theta < 118.5^\circ$ mainly S_2 , otherwise mainly S_1) and consequently both S_1 and S_2 are populated by the initial delta pulse. Because the CI is located right at the Franck-Condon region, IC takes place immediately after excitation. Another interesting feature of the PESs is the location of singlet-triplet interaction regions, favouring ISC (see figure 6). Firstly, the intersection of S_1 and T_3 circularly surrounds the S_2/S_1 CI and the Franck-Condon region. Therefore, all trajectories leaving the Franck-Condon region are forced to pass through this intersection. There, the spin-orbit coupling elements are on the order of 30 cm^{-1} and thus able to transfer a re-

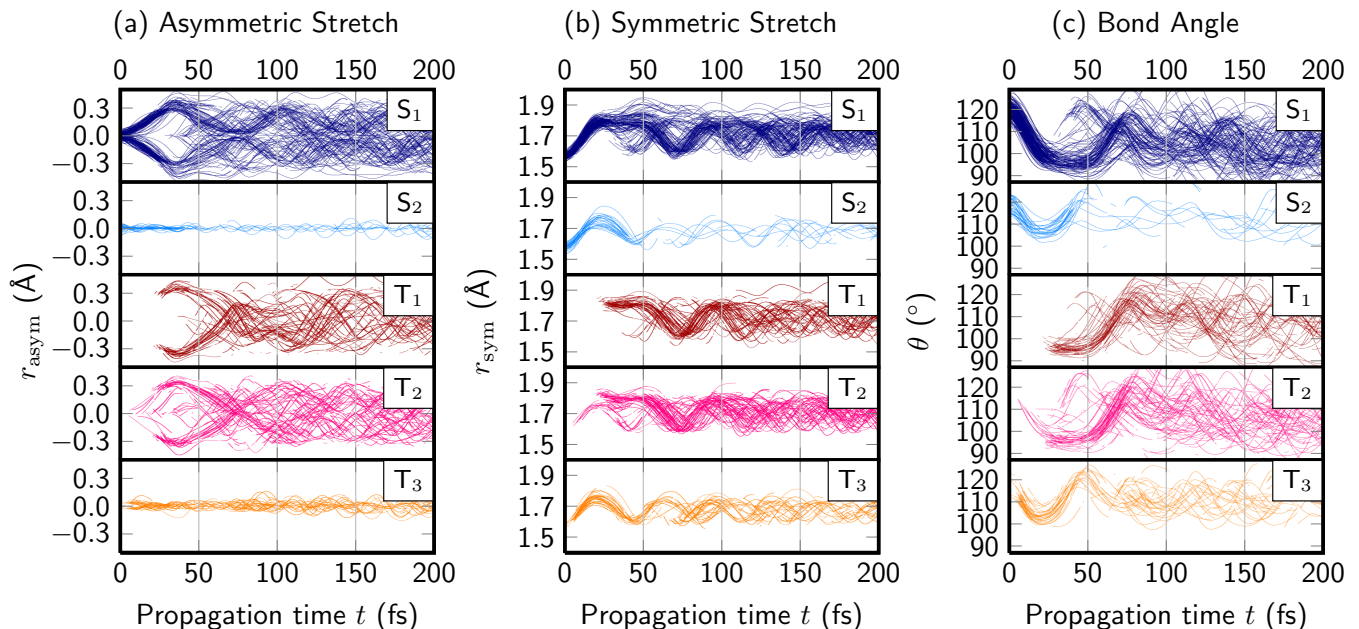


FIG. 8. Evolution of the internal coordinates of all trajectories during the first 200 fs.

markably large number of trajectories to the triplet PES. Secondly, the regions of proximity of S_1 and both T_1 and T_2 coincide with the outer turning point of the S_1 asymmetric stretch mode, see Figure 3 (b). Since at the turning point the potential is rather flat, the trajectories spend a long time in this region after excitation of the asymmetric stretch mode. Also in this region the spin-orbit couplings amount to about 30 cm^{-1} and allow for a noteworthy ISC yield. Since in this part of the PES S_1 , T_1 and T_2 all become very close in energy, simultaneous ISC to T_1 and T_2 becomes possible.

B. Spectrum

As can be seen in Figure 4, both transitions $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ contribute to the spectrum to a similar extent. The resulting calculated absorption spectrum is in reasonable agreement with the experimental one, although small deviations are patent. First, the calculated overall band shape is slightly red-shifted, by approximately 0.1 eV. This may be attributed to the double-zeta quality of the basis set since preliminary calculations indicate that larger basis sets give slightly higher excitation energies for all considered excited states. Despite its lesser accuracy, the double-zeta basis set was employed for the sake of computational performance during the dynamics.

Second, while the high-energy slopes of both spectra are quite similar, the low-energy slope of the calculated spectrum features too high intensities. In the experimental spectrum, at around 3.8 eV the absorption is already close to zero, while in the calculated spectrum the slope

extends until 3.5 eV. It is noteworthy that the experimental 0-0 transition for this band has been located at around 3.46 eV,⁵⁴ so the obtained excitation energies are plausible and only the intensities are overestimated.

Finally, it is obvious that the vibrational structure of the spectrum is not reproduced by our simulation. A description of this phenomenon goes beyond of the scope of this work, since it requires a quantum-mechanical treatment of the nuclear motion. A semi-classical simulation cannot account for quantization of the vibrational energy levels and also is not able to deliver nuclear wavefunction overlaps, which are necessary to obtain Franck-Condon factors. Thus, a correct calculation of the total absorption is not possible within this approach. The absence of the Franck-Condon factors might also explain the too intense low-energy slope in the calculated spectrum.

In conclusion, given the employed theoretical model, the simulated spectrum is in good agreement with the experiment and confirms the correctness of the initial conditions.

C. Dynamics in the singlet-manifold

A good agreement is obtained between the QD simulation by Müller and Köppel⁶ and our singlet-only MD simulations (recall Figure 5). Right after excitation, the states S_1 and S_2 briefly interact while still in proximity to the CI. However, already after ca 10 fs the population on S_1 has moved sufficiently far away from the CI to cease $S_1 \rightarrow S_2$ population transfer. Afterwards, only the S_2 population stays close to the interaction region, since the cone focusses the population on the intersec-

tion. Consequently, between 10 fs and 60 fs a decay from S_2 to S_1 is found. At 60 fs, the S_2 surface is completely depopulated in both QD and MD simulations.

The use of CASSCF in the QD simulation and of MRCI in the MD simulation lead to differences in the potentials' slopes, non-adiabatic coupling strengths and the exact location of the CI. Already Katagiri et al.⁴² noticed that the CASSCF method gives unsatisfactorily flat potentials of the S_1 state near the O–S...O dissociation limit. On the contrary, the dissociation energy as obtained on the MRCI level of theory (about 5.8 eV) is very close to the experimental one at 5.65 eV. The small discrepancies in the populations of the two simulations can be explained in this way.

After 70 fs (QD) or 80 fs (MD), the population on the S_1 surface returns to the S_1/S_2 intersection area in the Franck-Condon region. At this point, the S_2 is partly repopulated, though the initial population is not reached in both simulation types. This is reasonable in the sense that the ensemble already exhibits a considerable spread and the CI is missed by part of the ensemble.

In both studies, the wavepacket/ensemble basically moves all the time in S_1 , despite having sufficient energy to reach the S_2 . This behaviour can be attributed to the wavepacket/ensemble avoiding the CI because of the surrounding double-minimum potential (see figure 3). Following the potential energy gradient, the wavepacket/ensemble moves into regions of $r_1 \neq r_2$, where the two surfaces avoid each other and the non-adiabatic coupling is small. Also, both studies show that for times after 80 fs a coherent motion is virtually lost. Note that the experiment (see paper I) indicates a long-lived coherent motion. Although we could only speculate about the reasons for this disagreement in the QD case, we attribute the discrepancies between experiment and our MD results to our approximate MRCI gradients (see section IID). We are aware of the shortcomings of these gradients, however, MRCI potentials are necessary to qualitatively the SO_2 dynamics and these gradients are the best approximation currently available compatible with the SHARC methodology.

To sum up the findings so far, it is shown that the semi-classical dynamics gives results in satisfying agreement with the quantum dynamical results of Müller and Köppel. Both show a high population of S_1 at all times, with a fraction of the population oscillating between the two surfaces.

D. Dynamics in the singlet-triplet manifold

One of the most important results of this study is that the inclusion of triplet states leads to a completely different picture than that obtained in the singlet-only dynamics. ISC plays a significant role in the deactivation of SO_2 and, as can be seen from figure 6, ISC even competes with IC on a timescale of tens of femtoseconds. Experimental results of paper I (figure 6 (d)) also hint at the

participation of ISC in the ultrafast dynamics of SO_2 .

The differences between the singlet-only and the singlet-triplet dynamics are discussed in detail in the following. Already during the first 5 fs, in the singlet-only dynamics there is considerable population transfer between S_1 and S_2 close to the CI, while in the singlet-triplet simulation this exchange is almost absent. Instead, the S_1 population approaches the intersection with T_3 very fast and a large number of trajectories hop to the triplet surface.

The presence of T_3 also governs the fate of S_2 at later times. In the singlet-only simulation, S_2 is repopulated each time S_1 returns to the Franck-Condon region since the S_2/S_1 CI located there. In the singlet-triplet simulation, the S_1/T_3 intersection completely surrounds the CI and all trajectories returning to the Franck-Condon region have to pass through the singlet-triplet intersection. This leads to T_3 scavenging a large amount of incoming trajectories which could otherwise repopulate S_2 . It is mainly this mechanism which prevents S_2 from contributing significantly at later times.

However, the inclusion of the triplet states has its greatest impact on the dynamics on S_1 . This state acts as the central hub in the dynamics and directly interacts with all other excited states under consideration. Therefore, in contrast to the singlet-only case, the S_1 is heavily depleted by ISC. The large number of trajectories showing ISC can be rationalized by the fact that the S_1 interacts with the triplets over a wide range of geometries, while the singlet-singlet interaction is significant only in a very localized area (the CI).

The analysis of the net hops between the surfaces, presented in Figure 7, has been summarized in a global scheme (Figure 9) that collects the processes encountered in the photorelaxation dynamics of SO_2 . Each state is represented by a box, indicating also its respective initial population. The S_0 is absent from the figure, since relaxation to the ground state is unlikely in the time scales we are considering here.

The population transfer events have been divided into two sets. In the first set – the early transfers happening during the first 100 fs – mostly temporally localized events occur (solid arrows in the figure), while for later times we see the continuous population transfers (dashed arrows) of the second set. The temporal localization is caused by the trajectories moving collectively and passing jointly through the different interaction regions. For each localized transfer event, the effective time constant τ , the onset of this process and the percentage of the total population transferred in this event is given next to the corresponding solid arrow. Only major events are indicated. It is immediately obvious that S_1 interacts with all other excited states. It can also be seen that ISC and IC start instantly and consequently, both mechanisms act on an ultrafast timescale.

After approximately 100 fs, the ensemble of trajectories is considerably spread across the surfaces and therefore temporally localized events are not observed any-

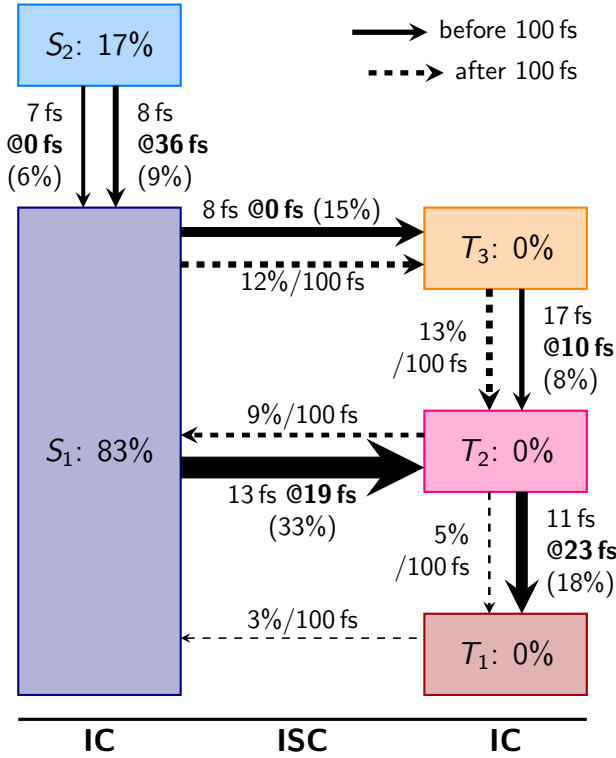


FIG. 9. Overview over transfer processes. The state boxes contain the initial relative population. Solid arrows denote the population transfers within the first 100 fs. The labels of these arrows give the rate constant τ , the onset (in bold) and the total population transferred during this process. Dashed arrows denote population transfer after the first 100 fs, where the labels give the rate of transfer.

more. Instead, we find a continuous transfer of population among a subset of the considered states. Circular population transfer between S_1 , T_3 and T_2 leads to a dynamical equilibrium. To a lesser extent, T_1 also contributes to the dynamical equilibrium by the alternative cycle $S_1 \rightarrow T_3 \rightarrow T_2 \rightarrow T_1 \rightarrow S_1$.

In view of the occurrence of localized transfer events and the mentioned circular transfer, a description of the whole dynamics by means of overall exponential fits is not suitable in the case of the relaxation dynamics in SO_2 .

Another very interesting feature of SO_2 , already noted in subsection III E with regard to figure 8, is the division of the considered PESs into two classes of PESs. States S_1 , T_1 and T_2 are characterized by a strong excitation of the asymmetric stretch mode because of their double-minimum potentials. On the contrary, the PESs of S_2 and T_3 do not allow any asymmetric stretch. What is most interesting about these two observations is that the nuclear motion, i.e. the vibrational frequency, does not allow for the identification of the populated electronic state. This fact may help to explain the experimental difficulty^{4,5} to observe the triplet states throughout decades of spectroscopic research.

In states S_1 , T_1 and T_2 , some trajectories show asymmetric stretch oscillations (figure 8 (a)) exclusively in one of the wells of the double-minimum potential (from $r_{\text{asym}}=0.0$ to around 0.4 \AA and back) with a period of about 70 fs. Another portion of the ensemble overcomes the central barrier and oscillates in both wells (from $r_{\text{asym}}=-0.4$ to $+0.4 \text{ \AA}$), with a full-cycle period of 140 fs. Interestingly, the oscillation period of 70 fs is also found in the symmetric stretch and bending modes (figure 8 (b) and (c)). Accordingly, the ensemble returns to the Franck-Condon region after this time interval and similarly at multiples of 70 fs.

From the spacing of the Clement's bands in the absorption spectrum^{1,30} (approximately 28 meV) one would expect a recurrence time of 148 fs. This time coincides with the asymmetric oscillation period across both potential wells found in the simulation, but is about double the first recurrence time of the ensemble in the Franck-Condon region. Our recurrence time of about 70 fs would lead to a spacing of 59 meV, which could in principle be hidden under the peaks spaced by 28 meV. In order to recover the relative experimental peak heights in the spectrum, the second recurrence needs to be more pronounced than the first one. We do not observe such a behavior. The reason is possibly that the ensemble is already too strongly dispersed prior to the second recurrence due to our approximate gradients. We believe that the oscillation period of 70 fs is correct, but is only due to a partial recurrence to the Franck-Condon region. Consequently, the expected peaks in the TRPEPICO (time-resolved photoelectron photoion coincidence) spectra of paper I might be hidden under the peaks corresponding to the 140 fs period. The full recurrence after these 140 fs is underestimated in our dynamics most probably because of the approximate gradients. Our rationale is supported by the findings of Leveque *et al.*⁷ published very recently. In their remarkable study, they discuss the role of the different spectroscopic states in detail and are able to achieve almost quantitative agreement with the experimental spectrum for the first time.

V. CONCLUSION

This work is – to the best of our knowledge – the first ab initio-based dynamics study to investigate the singlet-triplet interactions in sulphur dioxide. The comparison with singlet-only results from QD and ab initio MD reveals that the inclusion of the triplet states is essential in order to understand the photodynamics of this system. Due to the presence of singlet-triplet intersections at accessible sites on the PESs, not only ultrafast ISC processes have been found, but those strongly influence the singlet-singlet interaction.

After the initial delta pulse excitation, 80% of all trajectories start in the S_1 state and 20% in S_2 . While S_2 quickly decays to S_1 via a S_2/S_1 CI, in S_1 the asymmetric stretch mode is strongly excited. This stretch-

ing of the S–O bonds leads the trajectories inevitably through the intersection regions S_1/T_3 and slightly later $S_1/T_1/T_2$. Spin-orbit couplings on the order of 30 cm^{-1} are responsible for an efficient and ultrafast ISC in the regions of near-degeneracy. ISC together with IC between the triplet states is responsible for the establishment of a dynamical equilibrium after 100 fs. There, S_1 , T_3 and T_2 exchange population circularly, while S_2 and T_1 remain mostly static. The occurrence of ISC in our MD simulation fits nicely with the observation of signals attributed to quartet states in decay associated spectra in paper I.

It was also found that the PESs of S_1 , T_1 and T_2 on one hand and S_2 and T_3 on the other hand are sufficiently similar to cause indistinguishable molecular motion on these surfaces. This may explain the difficulties encountered in spectroscopic experiments to identify the participation of triplet states in the excited-state dynamics of SO_2 . We observed a dominant oscillation period of 70 fs in our simulation, which was related to the spacing of the Clement’s bands in the experimental absorption spectrum and the TRPEPICO spectra in paper I.

Thus we have shown that our recently developed ab initio molecular dynamics program SHARC²⁹ can provide significant insight into complex molecular processes including states of different multiplicities.

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